

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Process for the Purification of Finely Divided Oxides

We, DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, a body corporate organised under the laws of Germany, of 9 Weissfrauenstrasse, Frankfurt/Main, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to a process for the purification of finely divided oxides.

More particularly the invention relates to a process for the purification of finely divided oxides produced by the pyrogenic decomposition of volatile chlorides of metals and/or silicon, to produce oxides, oxide mixtures or mixed oxides, by the action of moist air flowing in countercurrent at elevated temperatures in a vertical treatment chamber or zone.

It is known that finely divided oxides of metals or silicon can be produced by pyrogenic decomposition of the volatile chlorides in the gas phase. From the chemical point of view, this reaction may either be oxidative or hydrolytic. In practice, the hydrolytic reaction may be carried out for example by feeding the volatile chloride, together with gases whose combustion is accompanied by the formation of water, to a flame in which reaction takes place. If a mixture of different chlorides is used, genuine mixed oxides are formed. In cases where several chlorides are burnt separately but the products are coagulated together, oxide mixtures are formed. The corresponding oxides, oxide mixtures or mixed oxides are formed in dispersion in the gaseous combustion products, steam, atmospheric nitrogen and hydrogen. The finely divided oxide, oxide mixture or mixed oxide that is left fol-

lowing separation of the gas phase contains substantial quantities of hydrogen chloride absorbed in its highly active surface. In addition, chemically combined chlorine may still be present in cases where the reaction is incomplete. Oxides of this kind show a strongly acid reaction. The pH-value of a 4% aqueous dispersion is usually below 2. In order to make these products suitable for the purpose for which they are to be used, they have to be subjected to an after-treatment, i.e. to deacidification.

There are various methods for deacidifying the oxides. For example, deacidification can be carried out by treating the oxide with alcohol vapours in a fluidised bed. In this case, changes affecting the surface quality occur owing to the fact that the OH-groups in the oxide are esterified with the alcohol to form silicic acid esters.

It is also known that deacidification can be carried out by heat treatment at temperatures in a range from 200 to 500°C. with moist air in a rotating tube or in screw conveyors or on an endless steel belt. One disadvantage of this process is that these machines contain moving parts which are prone to failure in view both of the high temperatures and the corrosive atmosphere and frequently give rise to production stoppages.

In one advantageous modification of this process, deacidification is carried out with heat and moist air in a fluidised bed. The fluidised bed used for this purpose may either be operated in countercurrent or in parallel current, although it is preferably operated in parallel current. In this process, the oxide together with the warm moist air is fed to a fluidised bed from underneath. The fluidised

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layer moves upwards through the treatment zone, supported by the upwardly flowing moist air. The purified oxide is run off laterally from a settling zone broadened in cross-section, whilst the acid waste gases are removed at the upper end of the treatment chamber. The treatment chamber is equipped with an internal heating system in the form of quartz tubes provided with electrical heating coils. The requisite temperatures are in a range from 450 to 800°C.

The advantage of this parallel-current fluidised bed process is that in addition to deacidification the material is simultaneously graded into coarse particles which do not flow upwards with the ascending stream towards the upper outlet, and into fine particles which flow out from the broadened settling zone.

Unfortunately, it is not always possible in practice to draw off the purified oxides without entraining acid waste gases. However, even if only small quantities of acid waste gases accompany the outflow of material, the required lower pH-limit is exceeded and this can give rise to difficulties in various applications of the oxides.

In another known process, highly dispersed oxides are purified by introducing the oxides into the uppermost chamber of a vertical shaft furnace divided up into at least three chambers by gas-permeable intermediate trays or plates, in countercurrent to a hot flow of steam introduced into the lowermost chamber. The result is that the solid particles are whirled around in the uppermost chamber and are delivered through an overflow tube projecting into the fluidised material, into the next lowest chamber, in which the process is repeated the material passing to each following chamber through suitable overflow tubes until it is discharged.

Although it is possible by means of this process to draw off the oxides without entraining acid waste gases, a multi-chamber system, which is very wasteful of heat, is required in order to prevent the waste gases from being penetrated by entrained oxide particles. In addition, in order to guarantee the discharge of oxide particles through the overflow tubes precise control of the rate of flow of the steam moving in countercurrent is necessary to maintain a higher rate of flow around the gas throughflow openings in the intermediate plates than at the lower end of the overflow.

The present invention provides a process for purifying finely divided oxides, mixed oxides or oxide mixtures of metals and/or silicon obtained by reacting chlorides of these metals and/or silicon at elevated temperatures in the gas phase with hydrolytic or oxidising gases, wherein the oxide, mixed oxide or oxide mixture is introduced into a treatment zone heated to 400 to 600°C., in which it descends under gravity in counter-

current to an ascending stream of a mixture of steam and a gas which is inert to the oxide, the stream being preferably preheated to about 120°C., the rate of flow of the gas phase being kept at a level low enough to prevent the finely divided oxide from forming a fluidised bed.

Considerations based on heat technology led to the belief that fairly poor energy yields would be inevitable in comparison with convention fluidised bed techniques. However, it was surprisingly found that finely divided pyrogenic oxides could be purified with particular advantage providing treatment with the mixture of steam and an inert gas is carried out in an empty shaft in the manner prescribed by the present invention instead of in a fluidised bed by countercurrent or parallel current, as in conventional processes. The unpurified oxide is introduced at the upper end of a, for example, tubular heated treatment zone, in which it descends in countercurrent to an ascending stream of a mixture of steam and an inert gas. In the deacidification of extremely finely divided silicon dioxide produced from  $\text{SiCl}_4$  by means of flame hydrolysis, from a pH-value of 1.9 to a pH-value of 4, the energy consumption was reduced by 50% in apparatus of the same dimensions and with the same flow of material. The temperature required for treatment was reduced from the 600—800°C. commonly used in the fluidised bed process, to from 400 to 600°C. in the vertical tube process. In addition, better pH-values, i.e. greater deacidification, than is possible with the fluidised bed process, was obtained particularly in the case of high-surface oxides. A long-term test extending over several months showed that in addition deacidification is more uniform and production less prone to stoppages, in contrast to the excessively low pH-values were often encountered in the fluidised bed process.

In comparison with the hitherto preferred fluidised bed process, the vertical-tube countercurrent process according to the invention has the following advantages:

substantially greater economy in view of the fact that the energy requirement is halved; the constituent material of the apparatus used is subjected to less thermal stressing in view of the fact that the treatment temperature is reduced from the original 600—800°C. to from 400 to 600°C., which in turn lengthens the service life of the apparatus; the product is treated more moderately in view of the reduction in temperature, with the result that its quality is improved; deacidification is more extensive, particularly in the case of high-surface oxides, and more uniform, i.e. less susceptible to interruption. The apparatus used is more reliable in operation.

The treatment zone is with advantage in the form of a vertical, cylindrical tube

widened at its upper and lower ends. The object of widening the tube at its upper end is to reduce or prevent the discharge of material by reducing the rate of flow of the waste gases, whilst the object of widening the tube at its lower end is to promote product discharge.

The treatment temperature may be maintained by means of an externally mounted electrical resistance heating system or alternatively by an internal heating system in which hydrogen is burnt in two vertically adjacent burners at the lower end of the treatment zone, the burners being screened to prevent oxide from passing into the flame zone. In the latter case combustion of the hydrogen provides steam for the treatment.

The invention is illustrated by the following Examples:

#### EXAMPLE 1

(a) 154 kg/hour of finely divided silicon dioxide (BET surface about 200 m<sup>2</sup>/g) with a pH-value of 1.9\*, prepared by flame hydrolysis of SiCl<sub>4</sub>, are introduced into a vertical tube treatment zone of the above-described shape with a capacity of about 300 litres. A mixture of 12.5 Nm<sup>3</sup> of steam and 10 m<sup>3</sup> of compressed air at 1.5 atms., is fed in laterally at the lower end of the treatment zone. The compressed air is preheated in a heater to 120°C. A temperature of 400–600°C., is maintained inside the treatment zone by means of an externally mounted electrical resistance heating system (heating coils in quartz tubes). The purified product is discharged at the foot of the treatment zone, whilst the acid waste gas is run off at the upper end under a pressure of around 10 mm. water column below atmospheric. The heat output amounts to around 28 kWh. The purified silicon dioxide has a pH-value of 4.0\*.

(b) For comparison, the purification process is carried out under the same conditions as described in (a), but by one of the conventional parallel-current fluidised bed processes:

154 kg/hour of highly dispersed silicon dioxide (BET-surface about 200 m<sup>2</sup>/g) with a pH-value of about 1.9\*, prepared by flame hydrolysis of SiCl<sub>4</sub>, are introduced upwards into a cylindrical, approximately 300-litre-capacity fluidised bed in conjunction with a mixture of 12.5 Nm<sup>3</sup> of steam and 18 m<sup>3</sup> of compressed air at 1.5 atms. pressure. The compressed air is preheated to 120°C. A temperature of 600–800°C. is maintained inside the fluidised bed reactor by means of an externally mounted electrical resistance heating system (heating coils in quartz tubes). The upper end of the reactor consists of a funnel-shaped widened portion from which the purified silicon dioxide is laterally run off, whilst the acid waste gas is removed under pressure at the upper end of the bed

under a pressure of about 10 mm. water column below atmospheric.

In order to obtain a purified silicon dioxide with a pH-value of 4.0\*, a heat output of 57 kWh. is required in this case.

#### EXAMPLE 2

41 kg/hour of highly dispersed silicon dioxide (BET-surface about 200 m<sup>2</sup>/g) with a pH-value of 1.9\*, prepared by flame hydrolysis of SiCl<sub>4</sub>, are introduced downwards into an externally heated vertical tube treatment zone as described in Example 1. A mixture of 7.5 Nm<sup>3</sup> of steam and 8 m<sup>3</sup> of air at 1.5 atms. pressure is fed in at the lower end of the treatment zone. The air is preheated in a heater to 120°C. A temperature of 400–600°C., is maintained inside the treatment zone. The purified product is discharged at the foot of the reactor, the acid waste gas being removed at the upper end under a pressure of 10 mm. water column below atmospheric.

The purified silicon dioxide has a pH-value of 4.2\*.

#### EXAMPLE 3

5.0 kg/hour of titanium dioxide with a chlorine content of 1.05%, prepared from TiCl<sub>4</sub> in the vapour phase, are introduced downwards into a vertical tube treatment zone of approximately 20 litres capacity. The treatment zone is externally heated to 600°C., by means of an electrical resistance heating system. 1.2 Nm<sup>3</sup> of air saturated with steam at 90°C., flow in countercurrent to the titanium dioxide. The oxide discharged at the foot of the treatment zone has a chlorine content of less than 0.005%.

#### EXAMPLE 4

5 kg/hour of finely divided aluminium oxide with a high chlorine content and a pH-value in aqueous dispersion of 1.5\*, prepared from aluminium chloride in the vapour phase, are introduced into a vertical-tube treatment zone of approximately 100 litres capacity. The treatment zone is internally heated by the combustion of hydrogen in two vertically adjacent burners in the lower end of the treatment zone. A total of 1.2 m<sup>3</sup>/h of hydrogen per hour is burnt. The amount of air supplied to both burners comprises 2m<sup>3</sup>/h. The hydrogen flames are screened to prevent the finely divided oxide from entering the hot flame zone. The temperature of the combustion gases, nitrogen and steam, ascending through the treatment zone, is about 600°C. Another 2 m<sup>3</sup>/h of air are blown in at the foot of the treatment zone. The purified oxide issuing from the lower end of the treatment zone has a chlorine content of less than 0.005%. The pH-value of an aqueous

\* indicates pH measured in a 4% aqueous dispersion.

dispersion amounts to 8.2%. The surface of the oxide, approximately 80 m<sup>2</sup>/g, is unchanged.

WHAT WE CLAIM IS:—

5 1. A process for purifying finely divided oxides, mixed oxides or oxide mixtures of metals and/or silicon obtained by reacting chlorides of these metals and/or silicon at  
10 elevated temperatures in the gas phase with hydrolytic or oxidising gases, wherein the oxide, mixed oxide or oxide mixture is introduced into a treatment zone heated to  
15 400 to 600°C., in which it ascends under gravity in countercurrent to an ascending stream of a mixture of steam and a gas  
20 which is inert to the oxide, the rate of flow of the gas being kept at a level low enough to prevent the finely divided oxide from forming a fluidised bed.

2. A process as claimed in claim 1, wherein the stream of a mixture of steam and a gas inert to the oxide is preheated to about 120°C.

3. A process as claimed in claim 1 or 2, wherein the treatment temperature is maintained by means of an externally mounted electrical resistance heating system. 25

4. A process as claimed in claim 1 or 2, wherein the treatment temperature is maintained by means of an internal heating system in which hydrogen is burnt in two vertically adjacent burners at the lower end of the treatment zone, the burners being screened to prevent oxide from passing into the flame zone and the combustion of the hydrogen providing steam for the treatment. 30 35

5. A process as claimed in claim 1, substantially as hereinbefore described with reference to the Examples.

ELKINGTON AND FIFE,  
Chartered Patent Agents,  
High Holborn House, 52—54, High Holborn,  
London, W.C.1,  
Agents for the Applicants.

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